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(54) AGROHORTICULTURAL BACTERICIDE

(57) A primary object of the present invention is to provide a highly safe germicidal composition for agricultural and horticultural use which show excellent germicidal activity not only against ordinary bacteria and fungi but also against chemical-resistant bacterial and fungal strains. The germicidal composition of the invention comprises an aldonic acid copper salt as an active ingredient.

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Description

TECHNICAL FIELD

The present invention relates to a germicidal composition for agricultural and horticultural use.

PRIOR ART

Various germicides (bactericides/fungicides) have so far been used in agriculture and horticulture to control diseases of rice plants, vegetables, fruit trees, flowering plants and other crop plants. Typical examples among them are benomyl (generic name: methyl 1-butylcarbamoyl-2-benzimidazolcarbamate), thiuram (generic name: bis(dimethylthiocarbamoyl) disulfide), oxolinic acid and the like. However, there is a problem with such prior art pesticides that upon successive application thereof, strains resistant thereto develop, so that their biocidal effects are more or less counteracted in many instances.

On the other hand, copper-based germicidal formulations, which contain a copper compound, are characterized in that they are free of resistant strain development. Therefore, copper formulations containing cupric hydroxide, copper nonylphenolsulfonate or the like as an active ingredient are currently in general use. However, for achieving satisfactory germicidal effects using such prior art copper formulations, it is essential to use them in high concentrations; such use in high concentrations result in manifestation of phytotoxicity and cause leaf burn and other injuries, hence is undesirable.

Furthermore, concern about environmental problems is increasing nowadays. In view of these, it is highly desirable that a safer germicide for agricultural and horticultural use be developed.

DISCLOSURE OF INVENTION

It is an object of the present invention to provide a germicidal composition for agricultural and horticultural use which shows excellent germicidal effects not only on general bacteria and fungi but also on drug-resistant microbial strains and is effective in controlling disease damages to crop plants in much lower concentrations as compared with the conventional copper formulations.

Another object of the invention is to provide a germicidal composition for agricultural and horticultural use which will not cause chemical injuries such as leaf burn.

A further object of the invention is to provide an environmentally safe germicidal composition for agricultural and horticultural use.

Other features of the present invention will become apparent from the description which follows.

In accordance with the invention, a germicidal composition for agricultural and horticultural use which comprises an aldonic acid copper salt is provided.

In the germicidal composition according to the present invention, an aldonic acid copper salt is used. The term "aldonic acid" is a general term for the compound derived, from a chemical formula viewpoint, from an aldehyde group-containing monosaccharide (aldose) by oxidation of said aldehyde group. As specific examples of the aldonic acid, there may be mentioned compounds derived from such monosaccharides as aldotrioses (e.g. D-glyceraldehyde etc.), aldotetroses (e.g. D-erythrose etc.), aldopentoses (e.g. D-ribose, D-xylose, L-arabinose, etc.) and aldohexoses (e.g. D-glucose, D-galactose, D-mannose, etc.) by oxidation of the aldehyde group thereof to a carboxyl group.

In the practice of the present invention, cupric (or copper(II)) gluconate is particularly preferred as the aldonic acid copper salt mentioned above. Said cupric salt is known as a food additive and very safe from an environmental viewpoint.

In the practice of the present invention, either one single aldonic acid copper salt or a combination of two or more aldonic acid copper salts may be used.

For attaining still minimized phytotoxicity, calcium carbonate may be added to the germicidal composition of the present invention. Furthermore, the germicidal composition of the invention may contain one or more of known insecticides, bactericides, fungicides, herbicides, fertilizers and like farm chemicals unless the effects of the invention are lessened.

Usable as insecticides are, for instance, cyanophos, fenthion, fenitrothion, dichlofenthion, pirimiphos methyl, diazinon, isoxathion, pyridafenthion, chloropyrifos methyl, chloropyrifos, vamidothion, malathion, phenthoate, dimethoate, thiometon, phosalone, phosmet, methidathion, prothiophos, sulprofos, profenofos, pyraclofos, dichlorvos, monocrotophos, naled, chlorfenvinphos, acephate, EPN, ethion, carbaryl, fenobucarb, etiofencarb, pirimicarb, carbosulfan, benfracarb, methomyl, thiodicarb, alanicarb, biphenthrin, permethrin, cypermethrin, cyhalothrin, cyfluthrin, fenpropathrin, tralomethrin, fenvalerate, flucitrinate, fluvalinate, ethofenprox, cartap, thiocyclam, bensultap, diflubenzuron, teflubenzuron, chlorfluazuron, flufenoxuron, buprofezin, fenoxycarb, benzoepin, imidaclopride, sodium oleate, kelthane, fensobromorate, tetradifon, propargite, amitraz, benzomate, fenothiocarb, hexythiazox, fenbutatin oxide, fenprioximate, tebufenpirad, pyridapen, clofentezin, polynactin complexes, and so forth.

Usable as bactericdes and/or fungicides are inorganic copper, oxine-copper, inorganic sulfur, sodium hydrogen carbonate, potassium hydrogen carbonate, captan, dichlofluanide, chlorothalonil, fusaride, iprovenfos, edifenphos, phosethyl, thiophanate methyl, benomyl, thiabendazole, iprodione, vinclozolin, procymidone, fluorimide, metalaxyl, oxadixyl, triadimefon, bitertanol, myclobutanil, hexaconazole, propiconazole, difenoconazole, iproconazole, imibenconazole, triflumizole, proclanoz, peflazoate, fenarimol, pirifenox, trifolin, UBF-910, dithianon, quinomethionate, dinocap, benthiazole, triazine, ferimuzon, fluazinam, dietofencarb, oxolinic acid, iminocutadine acetate, iminocutadine alvesilate, kasugamycin, polyoxin, streptomycin, oxytetracycline, cymoxanil, dimetomor, ICI A 5504, cresoxyme methyl, fludioxonil, mepanipyrim, pyrimetanil, cyprodinil, etc.

Usable as the herbicides are, for example, fluazifop, quizalofop ethyl, aloxydim, cetoxydim and the like.

The germicidal composition of the present invention may comprise the above-mentioned aldonic acid copper salt in powder form as such or may occur as an aqueous solution of the same.

In preparing the germicidal composition according to the present invention, the water species to be used is not limited to any particular one but may be, for example, tap water, deionized water, activated carbon-treated water or distilled water. The concentration of the aldonic acid copper salt is not limited to any particlar level but may generally be 0 to less than 100% by weight, preferably about 5 to 90% by weight.

Alternatively, the germicidal composition of the present invention, like the known copper formulations, may be prepared in the form of popular formulations such as spray formulations, wettable powders, emulsions, dusts, granules, etc. using appropriate carriers, surfactants and so on as necessary. Usable as the carriers are known ones such as clay, kaolin, bentonite, talc, acid clay, diatomaceous earth, calcium carbonate, nitrocellulose, starch, gum arabic, gaseous carbon dioxide, freons, benzene, kerosene, alcohols, acetone, xylene, methylnaphthalene, cyclohexane, animal fatty acid esters, potassium sulfate, potassium chloride, potassium nitrate, calcium dihydrogen phosphate, sodium sulfate, etc. Usable as the surfactants are known ones such as lecithin, sucrose fatty acid esters, sorbitan fatty acid esters, monoglycerides, polypropylene glycol fatty acid esters, soaps, higher alcohol sulfate esters, alkylsulfonic acid salts, quaternary ammonium salts, polyalkylene oxides, sodium ligninsulfonate, sodium alkylbenzenesulfonates, sodium dinaphthylmethanesulfonate, sodium lauryl alcohol sulfate, polyoxyethylene alkylaryl ethers, etc.

In applying the germicidal composition according to the present invention, known applicaiton methods can be widely employed. To be more concrete, such common methods as dipping, spraying, drenching arid the like can be employed. In applying to rice or such tuber plants as potato, paddy (unhulled rice) or seed potato is preferably subjected to dipping treatment. In the case of other crop plants, foliage application is preferred.

Prior to application to crop plants, the germicidal composition of the present invention is diluted with water or some other diluent to an appropriate concentration.

In applying the germicidal composition of the present invention to crop plants, the concentration of the active ingredient aldonic acid copper salt may be suitably selected within a wide range according to the crop plant to be treated, the disease to be controlled, the stage of growth of the crop plant to be treated and the method of treatment, among others. Thus, in the case of dipping treatment, for instance, a standard concentration is generally about 200 to 5,000 ppm (about 25 to 700 ppm as copper), preferably about 500 to 2,000 ppm (about 70 to 280 ppm as copper). In the case of foliage application, a standard concentration is generally about 50 to 2,000 ppm (about 5 to 280 ppm as copper), preferably about 250 to 1,000 ppm (about 30 to 140 ppm as copper).

The crop plant to be treated and the disease to be controlled with the germicidal composition of the present invention is not particularly limited but can include a wide variety. Thus, as concrete examples of the target crop plant, there may be mentioned, for example, rice, vegetables, fruit trees and flowering plants, and, as concrete examples of the target disease, there may be mentioned bacterial diseases as well as fungal diseases such as powdery mildew, late blight and downy mildew, among others.

The germicidal composition of the present invention is particularly effective against the following crop plant diseases.

Rice :	bacterial grain rot, bacterial seedling blight, bacterial brown stripe, "bakanae" disease (gibberella infection), Helminthosporium leaf spot, blast;
Cucumber :	bacterial spot, downy mildew, powdery mildew;
Tomato :	late blight, leaf spot;
Lettuce :	bacterial spot, bacterial soft rot, rot;
Spinach :	downy mildew;
Onion, Japanese radish, Chinese cabbage :	bacterial soft rot;
Melon :	angular leaf spot, downy mildew, powdery mildew;
Cabbage :	black rot, bacterial soft rot, powdery mildew;
Carrot :	leaf blight;
Potato :	late blight, scab;
Citrus :	canker, greasy spot, melanose;
Grape :	downy mildew, rust;
Kiwi fruit :	bacterial blossom blight, canker;

Cherry :	short hole;
Japanese apricot :	bacterial canker;
Peach :	bacterial short hole;
Tea plant :	bacterial shoot blight, anthracnose, net blister blight, blister blight;
Hop :	downy mildew;
Rose :	powdery mildew.

The germicidal composition of the present invention is also effective in controlling pasthogenic microorganisms in nutrient solutions in nutriculture.

The germicidal composition of the present invention is particularly effective against such pathogenic microorganisms as Erwinia species, Pseudomonas species, Xanthomonas species and like bacteria and mastigomycotina species and like fungi.

The germicidal composition of the present invention shows an excellent germicidal effect not only upon ordinary bacteria and fungi but also upon strains resistant to chemicals.

The germicidal composition of the present invention is effective in preventing disease damages to crop plants at markedly reduced concentrations as compared with the prior art copper preparations.

The germicidal composition of the present invention, upon application thereof, will not cause any chemical injury.

The germicidal composition of the present invention is very low in environmental safety.

BEST MODES FOR CARRYING OUT THE INVENTION

The following formulation example, working examples and comparative examples are further illustrative of the present invention.

Formulation Example 1

A germicidal composition according to the present invention with an active ingredient concentration of 50% was prepared by admixing 50 parts by weight of cupric gluconate with 50 parts by weight of water.

Example 1 (rice bacterial seedling blight control test)

The germicidal composition of the invention as prepared in Formulation Example 1 was diluted with water to the active ingredient concentration indicated below in Table 1. The dilution was placed in a 100-ml beaker and 10 g of paddy infected with the causative microorganism of rice seedling blight was immersed therein for 24 hours. The thus-treated paddy was presoaked at 20°C for 3 days, then stimulated for germination at 32°C for 1 day, and sowed into a 12 x 12 cm plastic case. The sown case was maintained in a greenhouse at a temperature of 32°C for 2 days and then seedlings showing disease symptoms were counted 2 weeks after sowing. The control percentage was calculated as follows:

$$\% \text{ Control} = (\text{number of diseased seedlings in no treatment plot} - \text{number of diseased seedlings in treatment plot}) / (\text{number of diseased seedlings in no treatment plot}) \times 100$$

For comparison, two germicides (wettable powders) available on the market were also tested in the same manner. The results obtained are shown in Table 1.

Table 1

Germicide	Active ingredient concentration (ppm)	Copper concentration (ppm)	% Control	Phyto toxicity
Germicide of invention	1000	140	80	None
Kocide Bordeaux	307	200	61	None
Starner	1000	-	44	None
No treatment	-	-	0	None
Kocide Bordeaux (tradename; active ingredient: cupric hydroxide) Starner (tradename; active ingredient: oxolinic acid)				

Example 2 (rice seeding rot by bacterial grain rot pathogen control test)

The procedure of Example 1 was followed except that paddy infected with the causative microorganism of rice bacterial grain rot was used and diseased seedlings were counted 3 weeks after sowing. The control percentahe was calculated as decribed in Example 1. The results are shown in Table 2.

Table 2

Germicide	Copper concentration (ppm)	% Control	Phytotoxicity
Germicide of invention	140	97	None
Kocide Bordeaux	200	81	None
Sterna	-	97	None
No treatment	-	0	None

Example 3 (cucumber bacterial spot control test)

The germicidal composition of the present invention as prepared in Formulation Example 1 was diluted with water to the active ingredient concentration indicated below in Table 3. A cucumber seedling at the single true leaf stage planted in a black vinyl pot was sprayed with 5 ml of the dilution and, 5 hours later, it was inoculated with the causative microorganism of cucumber bacterial spot by spraying. This cucumber seedling was kept under high-humidity conditions at 25°C for 7 days and then the area of lesion on the diseased leaves was determined and the lesion area percentage was calculated. The control percentage was calculated using the expression shown below. For comparison, two germicides available on the market were also tested in the same manner. The results obtained are shown in Table 3.

% Control = (lesion area percentage in no treatment plot - lesion area percentage in treatment plot)/(lesion area percentage in no treatment plot) x 100

Table 3

Germicide	Active ingredient concentration (ppm)	Copper concentration (ppm)	% Control	Phytotoxicity
Germicide of invention	500	70	80	None
Kocide Bordeaux	768	500	73	Leaf burn
Yonepon	600	58	10	None
No treatment	-	-	0	None
Kocide Bordeaux (tradename; active ingredient: cupric hydroxide) Yonepon (tradename; active ingredient: copper nonylphenolsulfonate)				

Example 4 (tomato late blight control test)

The germicidal composition of the present invention as prepared in Formulation Example 1 was diluted with water to the active ingredient concentration indicated below in Table 4. A tomato seedling at the four true leaf stage planted in a black vinyl pot was sprayed with 5 ml of the dilution and, 5 hours later, inoculated with spores of the causative microorganism of tomato late blight by spraying. This tomato seedling was kept under high humidity conditions at 25°C for 7 days and then diseased leaves were counted. The control percentage was calculated as indicated in Example 3. For comparison, a germicide available on the market was also tested in the same manner. The results obtained are

shown in Table 4.

Table 4

Germicide	Active ingredient concentration (ppm)	Copper concentration (ppm)	% Control	Phytotoxicity
Germicide of invention	500	70	73	None
	200	28	70	None
	100	14	61	None
Kocide Bordeaux	768	500	62	None
	307	200	60	None
	154	100	54	None
No treatment	-	-	0	None
Kocide Bordeaux (tradename; active ingredient: cupric hydroxide)				

Example 5 (cucumber powdery mildew control test)

The germicidal composition of the present invention as prepared in Formulation Example 1 was diluted with water to the active ingredient concentration indicated below in Table 5. A cucumber seedling at the single true leaf stage planted in a black vinyl pot was sprayed with 5 ml of the dilution and, 5 hours later, inoculated with spores of the benlate-resistant causa tive microorganism of cucumber powdery mildew by spraying. This cucumber seedling was kept in a greenhouse for 10 days and then diseased cucumber cotyledons were counted and the control percentage was calculated as indicated in Example 3. For comparison, two germicides available on the market were also tested in the same manner. The results obtained are shown in Table 5.

Table 5

Germicide	Active ingredient concentration (ppm)	Copper concentration (ppm)	% Control	Phytotoxicity
Germicide of invention	500	70	61	None
Kocide Bordeaux	768	500	30	Leaf burn
Benlate	500		35	None
No treatment	-	-	0	None
Kocide Bordeaux (tradename; active ingredient: cupric hydroxide) Benlate (tradename; active ingredient: benomyl)				

Example 6 (rice "bakanae" disease control test)

The procedure of Example 1 was followed except that paddy infected with the causative microorganism of rice "bakanae" disease was used and diseased seedlings were counted 4 weeks after sowing. The control percentage was calculated in the same manner. For comparison, two germicides available on the market were also tested in the same manner. The results are shown in Table 6.

Table 6

Germicide	Active ingredient concentration (ppm)	Copper concentration (ppm)	% Control	Phytotoxicity
Germicide of invention	2000	280	95	None
	1000	140	84	None
Kocide Bordeaux	214	143	47	None
Benlate T	2000	-	31	None
No treatment	-	-	0	None
Kocide Bordeaux (tradename; active ingredient: cupric hydroxide) Benlate T (tradename; active ingredients: benomyl and thiuram)				

Example 7 (Chinese cabbage bacterial soft rot control test)

The germicidal composition of the present invention as prepared in Formulation Example 1 was diluted with water to the respective active ingredient concentrations indicated below in Table 7. Japanese cabbage laminae injured with a bundle of needles were instantaneously dipped in one of the dilutions, air-dried and then inoculated with the causative microorganism of Chinese cabbage bacterial soft rot by placing on the needle lesion a paper disk impregnated with the causative microoganism. After maintaining in a plastic moist chamber for 4 days, diseased leaves were counted and the control percentage was calculated as indicated in Example 3. For comparison, a germicide available on the market was tested in the same manner. The results are shown in Table 7.

Table 7

Germicide	Active ingredient concentration (ppm)	Copper concentration (ppm)	% Control	Phytotoxicity
Germicide of invention	500	70	100	None
	200	28	100	None
	100	14	63	None
Kocide Bordeaux	768	500	100	Leaf burn
	307	200	100	Leaf burn
	154	100	63	None
No treatment	-	-	0	None
Kocide Bordeaux (tradename; active ingredient: cupric hydroxide)				

Example 8 (rice Helminthosporium leaf spot control test)

The procedure of Example 1 was followed except that paddy infected with the causative microorganism of rice Helminthosporium leaf spot was used and diseased seedlings were counted 3 weeks after sowing. For comparison, a germicide available on the market was also tested in the same manner. The results are shown in Table 8.

Table 8

Germicide	Active ingredient concentration (ppm)	Copper concentration (ppm)	% Control	Phytotoxicity
Germicide of invention	1000	140	87	None
Kocide Bordeaux	307	200	51	None
No treatment	-	-	0	None
Kocide Bordeaux (tradename; active ingredient: cupric hydroxide)				

Example 9 (rice blast control test)

The germicidal composition of the invention as prepared in Formulation Example 1 was diluted with water to the active ingredient concentration indicated below in Table 9 and the dilution was placed in a 100-ml beaker, and 10 g of paddy infected with the causative microorganism of rice damping-off was immersed therein for 24 hours. A portion of the thus-treated paddy was sowed onto a moistened filter paper placed in a petri dish and kept at 25°C for 3 days. Then, those grains of paddy on which formation of spores of the causative microorganism of rice blast (Pyricularia oryzae) were counted as diseased paddy grains and the control percentage was calculated as follows:

% Control = (number of diseased paddy grains in no treatment plot - number of diseased paddy grains in treatment plot)/(number of diseased paddy grains in no treatment plot) x 100

For comparison, a germicide available on the market was also tested in the same manner. The results thus obtained are shown in Table 9.

Table 9

Germicide	Active ingredient concentration (ppm)	Copper concentration (ppm)	% Control	Phytotoxicity
Germicide of invention	1000	140	100	None
Kocide Bordeaux	307	200	67	None
No treatment	-	-	0	None
Kocide Bordeaux (tradename; active ingredient: cupric hydroxide)				

Claims

1. A germicidal composition for agricultural and horticultural use which comprises an aldonic acid copper salt as an active ingredient.

2. A germicidal composition for agricultural and horticultural use as claimed in Claim 1, wherein said aldonic acid copper salt is cupric gluconate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP95/00915

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl^6 A01N37/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl^6 A01N37/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 4-128217, A (Lion Corp.), April 28, 1992 (28. 04. 92) (Family: none)	1 - 2
A	JP, 3-178969, A (Rohm and Haas Company), August 2, 1991 (02. 08. 91) &EP, 425143, A2	1 - 2

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family.

Date of the actual completion of the international search	Date of mailing of the international search report
July 14, 1995 (14. 07. 95)	August 8, 1995 (08. 08. 95)
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